ON THE PHOSPHORESCENCE OF THE URANYL SALTS.

BY EDWARD L. NICHOLS AND H. L. HOWES.

IN a recent paper[1] on the phosphorescence of the double salt uranyl ammonium sulphate, the following facts were established:

1. There is no appreciable change of color during decay.

2. The decay of phosphorescence is exceedingly rapid, the intensity falling to one thousandth of its initial value within .0035 second.

3. The very complex fluorescence spectrum at $-180°$ is identical in structure and relative distribution of intensities with that observed during the earlier and later stages of phosphorescence.

4. The curve of decay of phosphorescence differs from the prevailing type in that although as usual two successive processes are distinguishable, the second process is more rapid instead of being slower than the first.

The study of these phenomena has since been extended to several other typical uranyl salts, the curves of decay of which were determined by the method described in that paper and under conditions of excitation, etc., as nearly constant as possible. These curves of decay are of the same new type originally found in the uranyl ammonium sulphate. The two processes, as determined by the customary method of plotting $I^{-1/2}$ as a function of the time are indicated by straight lines differing from one another in slope and the second process has in all cases the steeper gradient. Later experiments in which the intensity of excitation was increased, revealed the presence of a third process not included within the interval of time covered by our earlier experiment.

STUDIES INVOLVING THE FIRST AND SECOND PROCESSES.

The curves shown in Figs. 1 and 2 are typical of the results obtained with all the salts under observation. They represent the decay of the phosphorescence of the following compounds:

Curve.	Substance.
1.	Uranyl ammonium sulphate
2.	Uranyl potassium sulphate
3.	Uranyl nitrate $+6H_2O$
4.	Uranyl sulphate
5.	Uranyl ammonium chloride

[1] Nichols, Proceedings of National Academy of Sciences, Vol. II., p. 328.

The initial intensity, under like excitation, varies greatly in the different salts as also, to some extent, does the rate of decay. It will be noted that the initial intensities of the ammonium and potassium sulphates

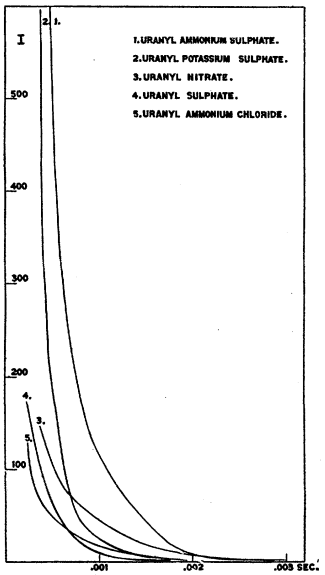

Fig. 1.

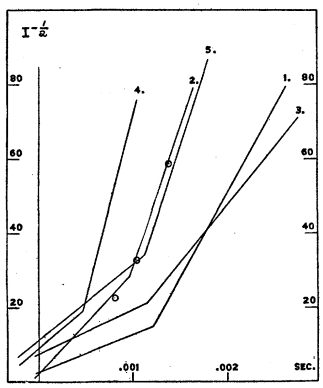

Fig. 2.

for example are several times greater than those of the nitrate, the sulphate and the ammonium chloride. This is however a question of previous history as well as of chemical and physical constitution as was determined in the following manner.

Uranyl potassium sulphate was dissolved in hot water and a mass of the minute crystals which were thrown down on cooling the solution were immediately sealed up in a glass tube. Care was taken throughout these manipulations to protect the precipitate from the action of light.

This sample, still in darkness, was mounted in the synchrono-phosphoroscope[1] and a curve of decay was taken, the first exposure to exciting light being that at the beginning of the run. The substance then showed temporarily, a brilliancy of phosphorescence much above that to be obtained under ordinary circumstances but was soon reduced to its normal and semi-permanent condition after which the usual curve of decay was obtained.

[1] For a description of this instrument, which was used in all the experiments recorded in this paper, except as otherwise stated, see the PHYSICAL REVIEW (2), VII., p. 586; also Science, V., XLIII., p. 937.

EXCITATION IN THE PRESENCE OF RED AND INFRA-RED RAYS.

To determine whether red or infra-red rays have an effect on these substances similar to that observed in the case of the phosphorescent sulphides a modification of the apparatus was made such that the surface under examination could be subjected to the intense illumination obtained by focusing the crater of an electric arc upon it. A screen of excellent ruby glass was interposed to cut off all but the longer waves and observations were made through a screen quite impervious to red.

Exposure to this source was found to affect measurably neither the brightness of fluorescence nor of phosphorescence nor the rate of decay. Curves taken after exposure to this source, those taken with the substance subjected to it interruptedly throughout the run, and curves in the determination of which readings were taken alternately with and without red light were all identical with those taken in entire absence from such exposures. The striking contrast between this negative result and the well-known effects of infra-red radiation upon the phosphorescence of the sulphides is notable.

The observations described in the note[1] already cited, showing the complete identity of the spectrum of fluorescence with that of phosphorescence seemed to indicate that the intensity would go over from that of fluorescence to that of phosphorescence without discontinuity. This conclusion was confirmed, within the errors of observation, by measurements just before and after the close of excitation. The only previous instances where this relation has been experimentally established so far as we know are to be found in Waggoner's[2] studies of phosphorescence of short duration and in our recent paper on the luminescence of kunzite.[3]

Where, as in these measurements, determinations have to be made through a very wide range and at exceedingly low intensities, doubts naturally arise as to the accuracy of the data for the lowest values. That in the present case the foot of the decay curves, where the brightness is reduced to a few thousandths of the initial intensity, is determined with a precision of the same order as that for higher values may be seen from Fig. 3 (Curve *BB*), in which the portion of the decay curve applying to the second process, *i. e.*, from .001 second onward, is plotted on a scale in which the ordinates for intensity are multiplied by ten. It will be noted that the observations fit the curve as closely as can be expected in work of this character. This is a fact quite in accord with previous

[1] Nichols, I. c.

[2] Waggoner, PHYSICAL REVIEW, XXVII., p. 209.

[3] Nichols and Howes, PHYSICAL REVIEW (2), IV., p. 26.

experiences in the domain of luminescence where observations made at the very lowest intensities which would permit of distinguishing the pattern in the contrast field of a photometer or spectrophotometer have been found quite as reliable as those in which the illumination was much more intense.

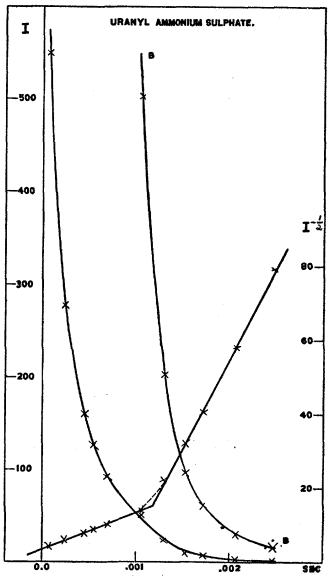

Fig. 3.

In view of the unexpected character of the decay curves for the phosphorescence of the uranyl compounds, the question arises whether the rather unusual mode of excitation employed; *i. e.*, periodically repeated exposures, 120 times a second to groups of sparks of high frequency, might produce such a result or whether the decay curves are characteristic of this class of compounds whatever the mode of excitation. It is true that both Waggoner[1] and Zeller[2] using a Merritt phosphoroscope found in their studies of phosphorescence of short duration that excitation by means of a spark discharge very similar to our own gave decay curves of the usual type.

It is also obvious from the measurements already described that the interval between excitation in our experiments, *i. e.*, 1/120 second is sufficient for the complete discharge of the phosphorescent glow and since the absence of any effect of red and infra-red indicates that there is no storage of undeveloped energy to be carried over, such as occurs in the phosphorescent sulphides, it seems probable that the decay curves do not vary greatly from that which might be obtained, were it possible to make the experiment, from a single exposure.

To test this a run was made upon the sample of uranyl ammonium sulphate previously used but with the Merritt phosphoroscope.

By driving the disk of this instrument 3,000 revolutions a minute, much the same range of time intervals was available as with the synchrono-phosphoroscope.

To further vary the conditions a quartz mercury arc was substituted for the spark gap of Waggoner and Zeller. The arrangement of apparatus was as shown in Fig. 4 in which *DD* is the revolving disk, *H* the mercury lamp, *P* the phosphorescent substance, *LB* the Lummer-Brodhun cube of

[1] Waggoner, PHYSICAL REVIEW, XXVII., p. 209.

[2] Zeller, PHYSICAL REVIEW, XXXI., p. 367.

the photometer, *SS* a color filter and milk glass screen. The device for shifting the oblique mirror *M* with reference to the aperture *A* in the disk is not shown.

Although the decay was somewhat more rapid in this determination on account of the less intense excitation; the curve was of precisely the type obtained by the previous method.

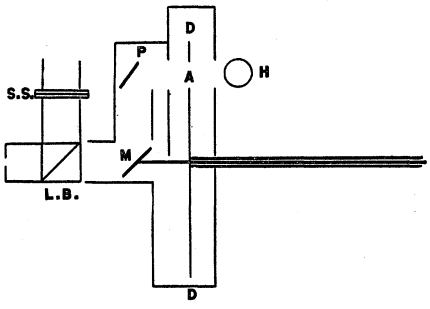

Fig. 4.

Measurements upon some of the bands of brief duration in the spectrum of the phosphorescent sulphides, recently made with the synchrono-phosphoroscope under experimental conditions identical with those described in this paper[1] yield curves of the usual type associated with these sulphides; so that the question of the change of form being due to the method employed is effectually eliminated. It is proposed, however, to further test the possible influence of the mode of excitation and method of measurement. For this experiment a phosphoroscope of the drum type, to be driven at very high speeds, is under construction.

SOLID SOLUTIONS AND SEMI-FLUIDS.

The uranyl salts differ from nearly all if not all phosphorescent substances hitherto studied. We do not have, as in the phosphorescent sulphides, the preparations of Waggoner, the ruby, etc., to deal with a trace of active material in solid solution but with compounds that are in themselves brilliantly phosphorescent. If the peculiar character of the curve of decay is due to that fact it might be expected that uranium glass, in which the active material is considered to be in a state of solid solution, would have a law of decay corresponding to the prevailing type for such solutions, *i. e.*, with the first process as indicated by the curve for $I^{-1/2}$ and time, represented by a line of steeper slope than the line for the second process. A piece of uranium glass gave, however, a decay curve similar to those of the uranyl salts (see Fig. 5). Another preparation which differs from most of the uranyl salts is the uranyl sodium phosphate, a sample of which was made by D. T. Wilber for certain studies in fluorescence recently published.[2] This substance is a very viscous liquid with the characteristic green fluorescence of the uranyl compounds.

[1] Nichols, Proc. Nat. Acad. Sciences, (1917).

[2] Howes and Wilber, PHYSICAL REVIEW (2), Vol. 7, p. 394, Mar., 1916.

Being a liquid one might expect, in accordance with the findings of Becquerel for liquids in general,[1] that there would be no observable after-glow. It is true that Bequerel expressed the belief that with a phosphoroscope of sufficient speed, phosphorescence would probably be detected in fluorescent liquids but no one, so far as we know, save Dewar in an unconfirmed statement concerning a supposed phosphorescence of liquid air, has since that time (1859) recorded an instance of phosphorescence excepting in solids and gases.

When a tube containing the phosphate was tested with the synchrono-phosphoroscope no phosphorescence was found of duration sufficient to be detected. Another sample so prepared as to reduce the amount of water to a minimum did however exhibit phosphorescence of measurable duration. This preparation, so slow was its rate of flow, might be regarded as a plastic solid rather than a viscous liquid. A bead of microcosmic salt, colored in the usual manner with uranium oxide, was comparable in its phosphorescence with canary glass.

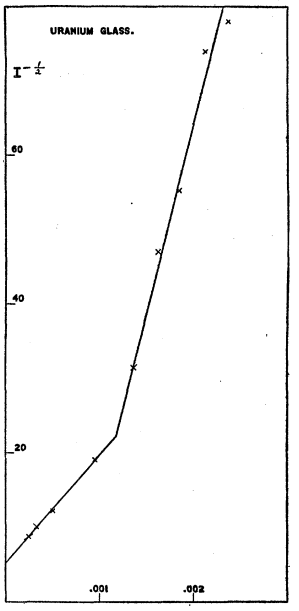

Fig. 5.

It appears that the persistence of luminescence is due to the consistency of the substance and disappears as the fluidity increases; also that the peculiar type of decay here described is common, not only to the crystalline uranyl salts in general but also to the gelatinous forms, as in this double salt and to substances in which uranium appears in solid solution as in the case of the canary glass.

THE THIRD PROCESS.

E. Becquerel[2] in the course of his great pioneer work on phosphorescence made a number of observations on the uranyl salts and on uranium glass. He noted the brilliant initial intensity and very rapid decay and to test the independence of the constant in his equation of decay when the illumination varied he made many measurements. If from his data we compute $I^{-1/2}$ as a function of the time we obtain curves of the same general form as those in Fig. 2.

Becquerel's observations are not numerous enough, taken by them-

[1] See E. Becquerel, La Lumiere, Vol. I., chapter on Phosphorescence.

[2] E. Becquerel, Annales de Chimie et de Physique (3), LXII., p. 1, 1861.

selves, to determine completely the type of curve. His measurements, however, cover a larger time interval than ours and the values for the longest times indicate an even more rapid decay following the second process. We had indeed found some indications of a similar tendency which had been omitted from our curves as lying almost beyond the range of definite determination.

To investigate the further trend of the curves of decay the intensity of excitation was increased by readjustment of the sparking circuit by which means it was found possible to extend the time interval for more than .006 sec. beyond the cessation of excitation.

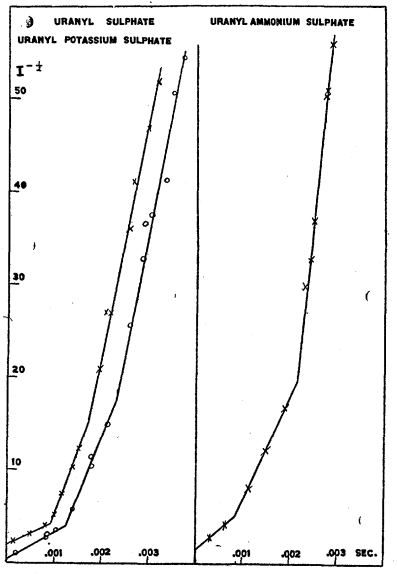

Fig. 6.

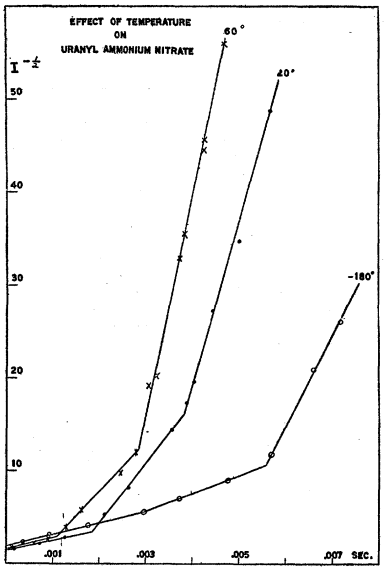

Fig. 7.

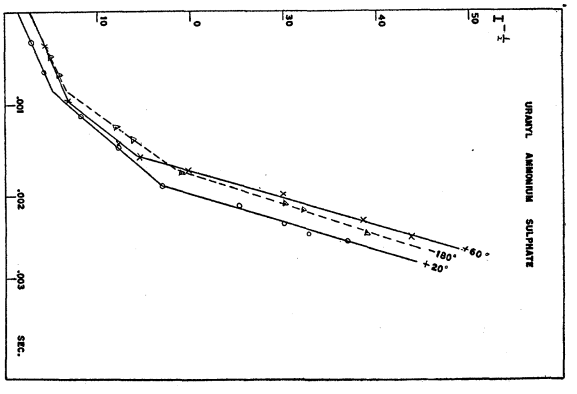

Fig. 8.

Careful, often repeated measurements, of the various salts showed in fact a third linear process beginning where our previous determinations had ceased and having a steeper slope, indicative of still more rapid decay. Typical results are indicated in Figs. 6, 7, 8, etc.

These processes may be numbered for convenience 1, 2 and 3 in the order in which they occur. Processes 1 and 2 are in general of about equal duration for a given salt. The abruptness of transition, however, varies greatly, and in some instances the change of slope is so gradual as to encroach seriously on process 2 at both ends.

THE INFLUENCE OF TEMPERATURE.

The only previous instances of decay of phosphorescence in which the later stages are more rapid than those preceding are noted by Ives and Luckiesh[1] in their study of the influence of temperature on phosphorescence, and by E. H. Kennard[2] in a more recent paper.

Ives and Luckiesh measured the phosphorescence of one of Lenard and Klatt's sulphides (BaBiK from Leppin and Masche). This substance was found to be very sensitive to change of temperature and the results at 0° C., 22° and 35°, when plotted for $I^{-1/2}$ any time in the usual manner, gave curves varying greatly in slope. The curve for 0 is concave towards the time axis, that for 22° linear and that for 35° *strongly convex*. They show that a linear relation may be obtained for each of these curves by varying the exponent of I.

The effect of temperature in the case of the phosphorescent sulphides, where one has to do with a composite of many overlapping bands of varying duration is undoubtedly different from that to be expected with the uranyl salts where the spectrum in spite of its complexity of structure is a unit. It was deemed of interest however to determine the effect of temperature upon the latter.

For this purpose a specimen of the uranyl ammonium nitrate was mounted within a cylindrical Dewar flask with unsilvered walls and its decay of phosphorescence was determined with the synchrono-phosphoroscope at a temperature a few degrees above that of liquid air (about −180°) at +20° and at +60°. The last-named temperature was maintained during the run by means of an electrical heating coil.

The principal change consists in a marked retardation of decay with lowering temperature (see Fig. 7), but this is not a universal characteristic of the uranyl compounds. Uranyl ammonium sulphate, for example (Fig. 8), is but slightly influenced in its rate of decay by change of tem-

[1] Ives and Luckiesh, Astrophysical Journal, XXXVI., p. 330 (1912).

[2] Kennard, PHYSICAL REVIEW (2), IV., p. 278 (1914).

perature and the curve for $-180°$ is intermediate between those for $+20°$ and $+60°$.

THE EFFECT OF VARYING THE INTENSITY OF EXCITATION.

To determine the effect of the intensity of excitation a series of measurements were made with the spark gap at various distances from the phosphorescent surface. The substance observed in these experiments was uranyl rubidium nitrate. It was found possible to make observations of the decay of phosphorescence with the excitation reduced to a two hundredth of that usually employed.

From the curves obtained of which four are given in Fig. 9, it will be

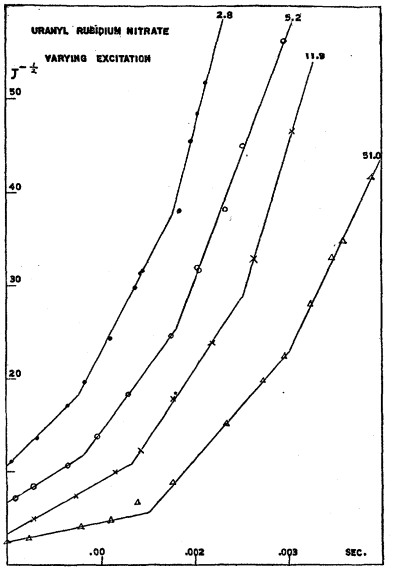

Fig. 9.

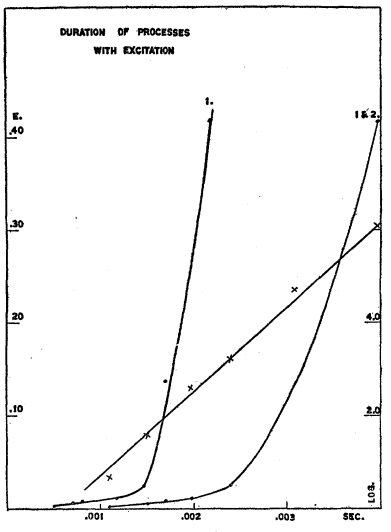

Fig. 10.

noted that all three processes are present whatever be the intensity of the exciting light; also that, taken roughly, processes 1 and 2 are of nearly equal duration and that with decreasing intensity of excitation the duration of each of these processes diminishes.

These relations are better shown in Fig. 10, in which the duration of process 1 and the sum of the durations of processes 1 and 2 counting from the close of excitation are plotted with the intensity of the exciting light as ordinates. Approximately in both cases the duration is proportional to the natural logarithm of the excitation. (See Table I.)

TABLE I.

Variation of Length of Processes with Excitation (Phosphorescence of Uranyl Rubidium Nitrate).

Intensity of Excitation (E).	Nat. Log E.	Duration.		
		Process 1.	Process 2.	Process 1 + 2.
41.70	6.033	.0022 sec.	.0018	.00400
13.70	4.919	.00170	.0014	.00310
2.52	3.220	.00147	.000993	.00240
1.35	2.590	.00118	.00080	.00198
0.900	2.190	.00080	.00090	.00170
0.476	1.560	.00070	.00076	.00146
0.201	0.698	.00050	.00060	.00110

This decrease in the duration of the two processes with falling excitation affords an obvious explanation of the varying character of the curves of decay of phosphorescent substances. Where the excitation is chiefly superficial, as in the case of some powders, the excitation may be nearly of one intensity and the curve made up of well-defined linear processes with sharp inflection points. We have found this to be the case in many instances. Where on the other hand fluorescence is excited within the crystalline mass by rays that have suffered considerable loss by absorption, etc., there will be a wide range of intensities of excitation and a curve results with distributed knees and linear processes shortened and sometimes almost obliterated. We observed this particularly where a clear crystal was mounted with faces perpendicular to the photometer and was excited from behind so that the light emitted by the surface nearest the exciting source passed through the crystal and was partially absorbed. Excitation occurred within the crystal in diminishing amount with increasing depth and the composite phosphorescence reaching the eue under such conditions showed this blending effect to a marked degree. The same crystal when excited from in front gave a curve in which the angles between processes were made more sharply defined. The effect in question is probably a general one and may well account for the perplexing differences in the curves of decay obtained under slightly varying circumstances. Thus one observer will obtain an angular curve where another, studying the same material, can detect no linear processes. The same observer, indeed, in attempting to repeat his measurements will often find the above-mentioned change of type under conditions which seem to be identical but in which the same relations as regards superficial and internal excitation are not preserved.

We found in the study of this effect a crystal one smooth face of which gave the blended curve while the opposite face, which was rough, gave

the angular curve, a change produced and reproducible by merely rotating the crystal through 180°.

THE PHOSPHORESCENCE OF VARIOUS NITRATES.

Observations were made on a series of nitrates previously prepared for the detailed comparison of the fluorescence spectra of that salt.[1] These consist of crystals with 6 H_2O (rhombic); 3 H_2O (triclinic) and 2 H_2O (system undetermined) as water of crystallization and a specimen sealed in glass which had been rendered as nearly anhydrous as was possible without decomposing the nitrate.

The curves of decay indicate a much slower rate of decay for the crystalline forms than for the anhydrous nitrate. Whatever effect the amount of water of crystallization may have is doubtless masked by the far greater influence of the crystalline form. This is perhaps to be expected since as has been shown in the paper just cited, these specimens exhibit as great differences in the structure and appearance of their fluorescence and absorption spectra as commonly exist between entirely distinct uranyl salts. That similar differences are found in the case of salts similar in composition but differing in crystalline form will be brought out in a forthcoming paper.

OBSERVATIONS ON POLARIZED PHOSPHORESCENCE.

Certain crystals of the double chlorides of uranyl exhibit fluorescence spectra consisting of sets of bands polarized at right angles to one another. To determine whether these components after the close of excitation decay independently or without change in their relative intensities, the following experiment was made.

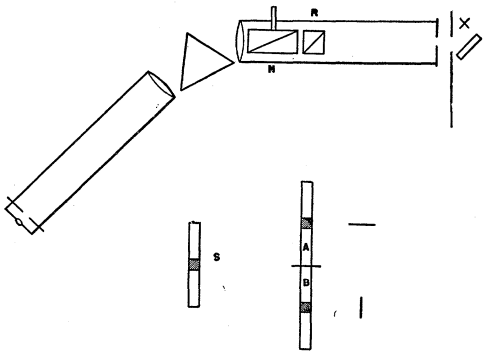

Fig. 11

A crystal of the rubidium uranyl chloride that exhibited the phenomenon of polarized fluorescence was mounted behind the disk of the synchrono-phosphoroscope and was observed with a spectroscope. The slit of the latter instrument was divided into two parts by means of an opaque strip across the middle (*S*, Fig. 11).

[1] Nichols and Merritt, PHYSICAL REVIEW (2), Vol. IX, p. 113 (1917).

Within the collimator a doubly refracting rhomb R and Nicol prism N were mounted. The rhomb gave two slit images vertically displaced and the adjustment was such that the lower part (A) of one image was contiguous with the upper part (B) of the other.

Thus two spectra of the phosphorescent field were obtained corresponding to the two polarized components. These presented the usual distinctive structures at whatever stage of the phosphorescent decay they were observed. By rotation of the Nicol prism the two fields could be brought to equal brightness for any given part of the spectrum and this balance, if made with the sector of the phosphoroscope set so as to give observations at .0005 second after extinction, was found equally correct up to .005 second or as long as phosphorescence was observable. The two components therefore decay at the same rate.

SUMMARY.

1. All uranyl salts thus far examined possess the same type of phosphorescence; *i. e.*, with increasing instead of diminishing rates of decay.

2. This is true not only of the crystalline forms but also of uranyl compounds in solid solution or in the plastic state characteristic of the double phosphates.

3. The initial brightness of phosphorescence under like excitation varies greatly with the different salts; as does also to some extent the rate of decay.

4. The brightness of a salt newly prepared in darkness is greater when first excited than subsequently but it soon reaches a nearly stable condition.

5. Exposure to red and infra-red rays is without effect as regards the rate of decay.

6. The phosphorescence, like the fluorescence of the uranyl salts appears to be independent of the mode of excitation and the structure of the intricate spectrum is the same during excitation and through the observable phosphorescent interval.

7. Changes in the rate of decay are not continuous but occur in definite steps there being at least three successive processes within the interval covered by observations, *i. e.*, about .006 seconds. These processes follow a law such that $I^{-1/2}$ is in linear relation to the time.

8. The first and second processes counting from the close of excitation are of nearly equal duration, increasing in duration with the intensity of excitation in such a manner that the duration of the process is approximately proportional to the natural logarithm of the excitation.

9. In certain salts, such as uranyl ammonium nitrate decay is retarded by cooling, in other cases the temperature effect is slight.

10. Uranyl nitrates with 2, 3 and 6 molecules of water of crystallization vary greatly in the rate of decay but the changes in crystalline form appear to be more important in this respect than the amount of water.

11. In the case of the polarized spectra of the double chlorides, both components decay at the same rate and no change in relative brightness could be detected throughout the range covered by observation.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
January, 1917.